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Molecular Electrocatalysts for Oxidation of Hydrogen Using Earth-Abundant Metals: Shoving Protons Around with Proton Relays

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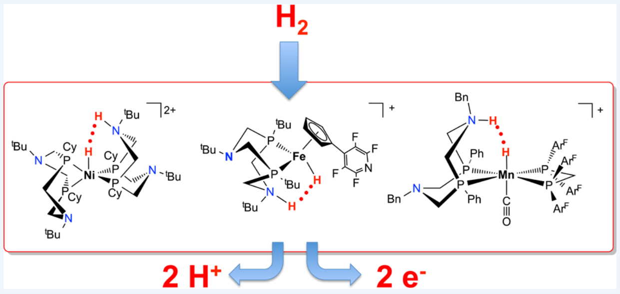

CONSPECTUS: Sustainable, carbon-neutral energy is needed to supplant the worldwide reliance on fossil fuels in order to address the persistent problem of increasing emissions of CO_2. Solar and wind energy are intermittent, highlighting the need to develop energy storage on a huge scale. Electrocatalysts provide a way to convert between electrical energy generated by renewable energy sources and chemical energy in the form of chemical bonds. Oxidation of hydrogen to give two electrons and two protons is carried out in fuel cells, but the typical catalyst is platinum, a precious metal of low earth abundance and high cost. In nature, hydrogenases based on iron or iron/nickel reversibly oxidize hydrogen with remarkable efficiencies and rates. Functional models of these enzymes have been synthesized with the goal of achieving electrocatalytic H_2 oxidation using inexpensive, earth-abundant metals along with a key feature identified in the [FeFe]-hydrogenase: an amine base positioned near the metal. The diphosphine ligands $P^{R}{}_{2}N^{R'}{}_{2}$ (1,5-diaza-3,7-diphosphacyclooctane with alkyl or aryl groups on the P and N atoms) are used as ligands in Ni, Fe, and Mn complexes. The pendant amines facilitate binding and heterolytic cleavage of H_2, placing the hydride on the metal and the proton on the amine. The pendant amines also serve as proton relays, accelerating intramolecular and intermolecular proton transfers. Electrochemical oxidations and deprotonations by an exogeneous amine base lead to catalytic cycles for oxidation of H_2 (1 atm) at room temperature for catalysts derived from $[Ni(P^{Cy}{}_{2}N^{R'}{}_{2})_2]^{2+}$, $Cp^{C_6F_5}Fe(P^{tBu}{}_{2}N^{Bn}{}_{2})H$, and $MnH(P^{Ph}{}_{2}N^{Bn}{}_{2})(bppm)(CO)$ [bppm = $(PAr^{F}{}_{2})_2CH_2$]. In the oxidation of H_2 catalyzed by $[Ni(P^{Cy}{}_{2}N^{R'}{}_{2})_2]^{2+}$, the initial product observed experimentally is a Ni(0) complex in which two of the pendant amines are protonated. Two different pathways can occur from this intermediate; deprotonation followed by oxidation occurs with a lower overpotential than the alternate pathway involving oxidation followed by deprotonation. The Mn cation $[Mn(P^{Ph}{}_{2}N^{Bn}{}_{2})(bppm)(CO)]^+$ mediates the rapid ($>10^4$ s^{-1} at -95 °C), reversible heterolytic cleavage of H_2. Obtaining the optimal benefit of pendant amines incorporated into the ligand requires that the pendant amine be properly positioned to interact with a M−H or $M(H_2)$ bond. In addition, ligands are ideally selected such that the hydride-acceptor ability of the metal and the basicity of a pendant are tuned to give low barriers for heterolytic cleavage of the H−H bond and subsequent proton transfer reactions. Using these principles allows the rational design of electrocatalysts for H_2 oxidation using earth-abundant metals.

■ INTRODUCTION

A shift away from burning of fossil fuels as our predominant energy source is needed in order to address the global problem of increasing emissions of CO_2.[1] Sustainable carbon-neutral energy is generated by the sun when it is shining and by the wind when it is blowing, but energy storage is critically needed because of the mismatch of when and where the energy is generated compared with when and where it is needed. Storing energy in chemical bonds (fuels) is attractive because of their high energy density. Electrocatalysis provides a means to interconvert chemical energy and electrical energy generated from renewable sources.

This Account describes our work on the design and development of molecular electrocatalysts for the oxidation of hydrogen. What is so difficult about tearing apart a small molecule like H_2? The loud, room-shaking sound resulting from lecture demonstrations when a flame combusts a H_2/O_2 balloon is vivid evidence that the energy content of the H−H bond is large and readily released. Controlling the oxidation to achieve energy efficiency is challenging, requiring management of the removal of two protons and two electrons. Fuel cells oxidize hydrogen, converting the chemical energy of the H−H bond into electrical energy and generating water, but they typically require platinum catalysts for the oxidation of H_2 at the anode and the reduction of O_2 at the cathode[2,3] (Figure 1).

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$$H_2 \rightleftharpoons 2\,H^+ + 2\,e^- \qquad \text{Oxidation of } H_2$$

$$^1/_2\ O_2 + 2\,H^+ + 2\,e^- \rightleftharpoons H_2O \qquad \text{Reduction of } O_2$$

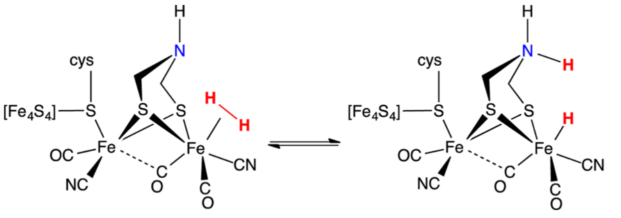
$$H_2 + {}^1/_2\ O_2 \longrightarrow H_2O$$

Figure 1. H_2 oxidation and O_2 reduction reactions (fuel cell).

The two reactions can be studied separately as half-cell reactions in electrochemical experiments, as described here. Questions have been raised concerning whether there will be enough Pt available just to meet future automotive needs, where most of the platinum is currently used in catalytic converters.[4] Along with low abundance, the cost of platinum is prohibitive for the huge scale needed for energy conversions. In addition, mining and purifying platinum requires much more energy (and generates more emissions) compared with earth-abundant metals. All of these considerations emphasize the need to develop catalysts based on earth-abundant metals.[5]

In contrast to platinum catalysts in fuel cells, hydrogen is produced and oxidized in nature by enzymes using only earth-abundant metals. Two enzymes studied in detail for H_2 oxidation and production are [NiFe]-hydrogenase and [FeFe]-hydrogenase.[6,7] The active site of [FeFe]-hydrogenase is shown in eq 1, but the drawing does not show the surrounding protein matrix, which influences its remarkable reactivity. A particularly intriguing feature identified in the [FeFe]-hydrogenase is the presence of an amine base near the metal. Our research on biologically inspired functional models of hydrogenase seeks to replicate the function of enzymes by designing molecular complexes that have similar reactivity rather than modeling the structural features[8−10] of the natural enzymes.

While this Account focuses on our efforts using earth-abundant metals and incorporating pendant amines that are designed to serve as proton relays, other groups have used a variety of successful approaches. Rauchfuss and co-workers have used redox-active ligands in Ir complexes[11] and reported structural models of [FeFe]-hydrogenase, including an iron complex that catalyzes the oxidation of H_2 using a chemical oxidant.[12] Ogo and co-workers have reported bimetallic complexes containing Ni and Ru that catalytically oxidize H_2,[13] including a paramagnetic nickel−ruthenium complex that heterolytically cleaves H_2 at room temperature, giving a Ni(μ-H)Ru complex that was characterized by neutron diffraction.[14] They discovered a functional mimic of the [NiFe]-hydrogenase that reacts with H_2.[15] Ogo and co-workers recently reported a new form of a [NiFe]-hydrogenase that was used in a fuel cell, with activity reported to surpass that of Pt.[16] The progress and challenges in the use of enzymes in fuel cells was reviewed by Armstrong and co-workers.[17] Progress toward earth-abundant catalysts continues to be moved forward by all of these diverse approaches.



(1)

TEARING H_2 APART AND RECRUITING PENDANT AMINES FOR THE HEAVY LIFTING

In a fuel cell, the electrons generate power, and the protons are used in the reduction of O_2 (Figure 1). In the half-cell electrochemical reactions discussed here, an amine base removes the protons, while the electrons are removed by the electrode. Our approach to the design of molecular electrocatalysts requires (1) reaction of H_2 with the metal complex, (2) heterolytic cleavage of H_2 into a proton and a hydride ion, and (3) removal of the two protons and two electrons (eq 2):

$$H_2 \longrightarrow H^+ + H^- \longrightarrow 2\,H^+ + 2\,e^- \qquad (2)$$

The amines incorporated into the second coordination sphere play a critical role, providing a parking place for protons before they are shuttled away from the catalyst by an exogenous base. The initially formed hydride is bound to the metal, so oxidations are needed to convert the metal hydride into a form that can be removed as a proton (Scheme 1).

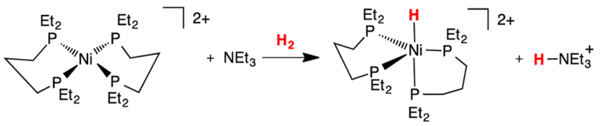
FROM INTERMOLECULAR H_2 CLEAVAGE TO INTRAMOLECULAR REACTIONS WITH PENDANT AMINES IN NICKEL COMPLEXES

Extensive studies of the thermodynamic hydricity of metal hydrides[18] suggested that $HNi(diphosphine)_2^+$ complexes were attractive for investigation as potential catalysts for oxidation of H_2. Addition of H_2 (1 atm) and NEt_3 to a solution of $[Ni(depp)_2]^{2+}$ (depp = $Et_2P(CH_2)_3PEt_2$) results in heterolytic cleavage of H_2 in a reaction involving an intermolecular proton transfer to NEt_3 from an (unobserved) complex with a bound H_2 (eq 3). Incorporation of an amine base into the diphosphine ligand to give a "PNP" ligand ($P^{Et}N^{Me}P^{Et}$ = $Et_2PCH_2N(Me)$-CH_2PEt_2) leads to rapid intramolecular heterolytic cleavage of H_2 (eq 4). Oxidation of H_2 (1 atm) is catalyzed by $[Ni(P^{Et}N^{Me}P^{Et})_2]^{2+}$ using NEt_3 as the exogeneous base, with an upper limit of 0.2 s^{-1} estimated for the turnover frequency.

The Ni−PNP moiety forms a six-membered ring and undergoes chair−boat conformational changes (cf. conformational changes in cyclohexane). The pendant amine is properly positioned to interact with a Ni−H or Ni(H_2) complex only when the ligand is in the boat conformation. In contrast, P_2N_2 ligands generally have one pendant amine in a boat configuration and positioned close to the metal, similar to the positioning of the azadithiolate ligand in [FeFe]-hydrogenase (eq 1), leading to faster catalysis. Scheme 2 shows the synthesis of and abbreviations used for P_2N_2 ligands.

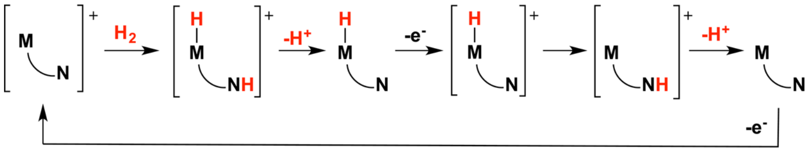
CLEAVAGE OF H_2 BY $[Ni(P^R{}_2N^{R'}{}_2)_2]^{2+}$: THE Ni GETS BOTH ELECTRONS AND THE PENDANT AMINES TAKE THE PROTONS

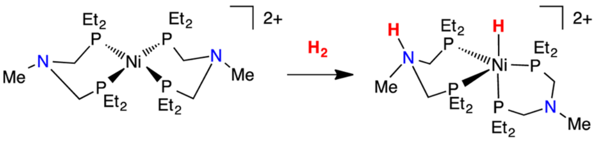
In contrast to the prevalence of dihydrogen complexes, M(η^2-H_2),[19] for many metals, only a few examples have been reported for Ni.[20−22] The reaction of $[Ni(P^{Cy}{}_2N^{R'}{}_2)_2]^{2+}$ (Cy = cyclohexyl; R′ = benzyl (Bn),[23,24] *tert*-butyl,[25] CH_2CH_2OMe[26]) with H_2 occurs rapidly, yet we never obtained spectroscopic evidence for $[Ni(P^{Cy}{}_2N^{R'}{}_2)_2(H_2)]^{2+}$, even when the reaction of H_2 with $[Ni(P^{Cy}{}_2N^{t\text{-}Bu}{}_2)_2]^{2+}$ was studied at −100 °C.[25] Instead, the Ni^{II} complex is reduced by H_2 to give a Ni^0 complex, and



(3)

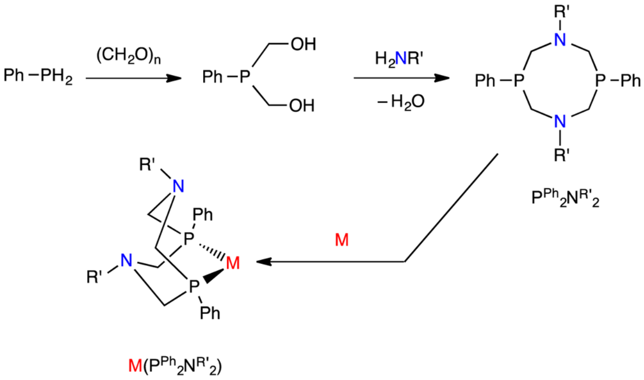
Scheme 1. General Scheme for Electrocatalytic Oxidation of H_2 Using a Metal Complex with a Pendant Amine





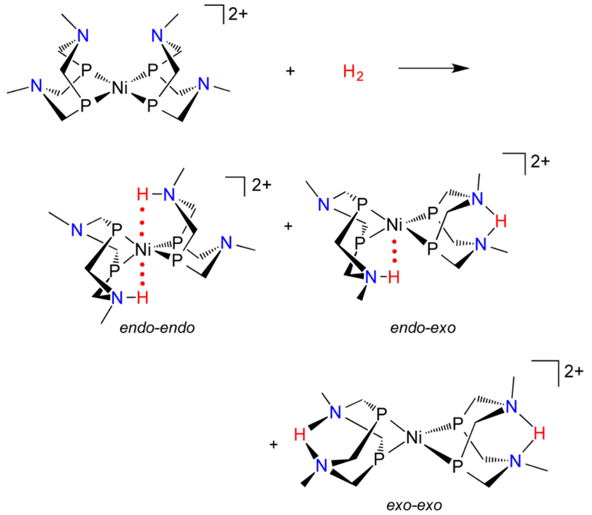
$[Ni(P^{Et}N^{Me}P^{Et})_2]^{2+}$

Scheme 2



the two protons are transferred to the pendant amines (eq 5). Only the *endo−endo* isomer is initially observed, but at higher temperatures, it equilibrates with the *endo−exo* and *exo−exo* isomers. The *endo−endo* isomer has two $Ni^0\cdots H-N$ hydrogen bonds, and the *exo−exo* isomer has two $N-H\cdots N$ hydrogen bonds in a "pinched" configuration; the *endo−exo* isomer has one of each. The three isomers are of similar energy, and further understanding was provided by electrochemical, thermochemical, and computational studies.[27]

Computations provided insight into intermediates in the reaction of H_2 with $[Ni(P^R{}_2N^{R'}{}_2)_2]^{2+}$ prior to the formation of the *endo−endo* isomer.[28] These ab initio molecular dynamics simulations provided evidence that a dihydrogen complex is initially formed; the loss of translational entropy of H_2 contributes significantly to the barrier to formation of the $Ni(\eta^2\text{-}H_2)^{2+}$ intermediate (Scheme 3). The dihydrogen complex cleaves H_2 heterolytically, resulting in an unobserved complex with nickel hydride and a protonated amine, which converts to the Ni(0) *endo−endo* complex. Computations showed that homolytic cleavage of the H−H bond to give a nickel dihydride, $[Ni(P^R{}_2N^{R'}{}_2)_2(H)_2]^{2+}$, would be of much higher energy. Detailed NMR spectroscopic experiments, coupled with computational studies, showed that intramolecular[29] proton transfer between the isomers can be rapid, about 10^4−10^5 s^{-1} at 25 °C. In contrast, intermolecular[30] proton transfers are generally much slower than intramolecular proton movement.



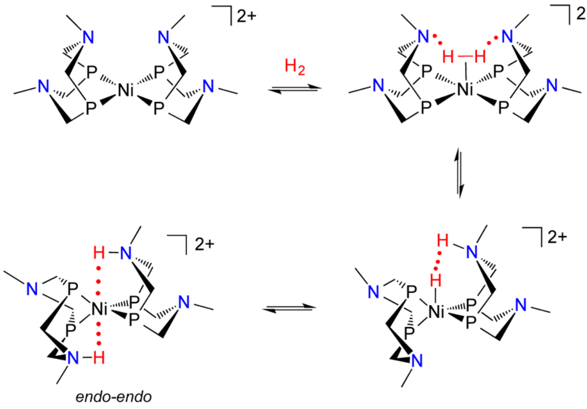
(5)

■ ELECTROCATALYTIC OXIDATION OF H_2 BY $[Ni(P^{Cy}{}_2N^{R'}{}_2)_2]^{2+}$

Electrocatalytic oxidation of H_2 (1 atm) is catalyzed by $[Ni(P^{Cy}{}_2N^{R'}{}_2)_2]^{2+}$ at room temperature. Thermochemical studies indicated that the free energy for addition of H_2 to $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2]^{2+}$ (eq 5) is $\Delta G^\circ_{H_2} = -3.1$ kcal/mol, and catalytic oxidation of H_2 using NEt_3 has a turnover frequency (TOF) of 10 s^{-1}.[23] Changing the substituent on the pendant amine from benzyl to the more electron-donating *tert*-butyl group makes the pendant amine more basic, leading to a more favorable $\Delta G^\circ_{H_2}$ of −7.9 kcal/mol for $[Ni(P^{Cy}{}_2N^{t\text{-}Bu}{}_2)_2]^{2+}$. In dry MeCN as the solvent with NEt_3 as the base, hydrogen oxidation is catalyzed by $[Ni(P^{Cy}{}_2N^{t\text{-}Bu}{}_2)_2]^{2+}$ with a TOF of 3 s^{-1} at 23 °C.[25] A higher turnover frequency (45 s^{-1}) was found when the same reaction was carried out with 0.86 M water. Similar TOFs were observed in dry MeCN using the smaller base *n*-$BuNH_2$, and added water had a minimal effect on the TOF with *n*-$BuNH_2$. These results imply that the larger steric profile of NEt_3 compared with *n*-$BuNH_2$ influences the rate and that water facilitates proton movement.[25,31]

Electrocatalytic oxidation of H_2 by $[Ni(P^{Cy}{}_2N^{(CH_2)_2OMe})_2]^{2+}$ with *n*-$BuNH_2$ occurs at $E_{cat/2} = -0.81$ V, with a TOF of 17 s^{-1} and an overpotential at $E_{cat/2}$ of 300 mV.[26] Using only water

Scheme 3



(and no amine) as the exogeneous base gives catalysis at a more positive potential of $E_{cat/2} = -0.48$ V, with a TOF of 5 s^{-1} and an overpotential at $E_{cat/2}$ of 720 mV. Figure 2 shows the enhanced current indicative of catalysis in the cyclic voltammograms at the two different potentials, using the strong (amine) or weak (H_2O) base. The complex $[Ni(P^{Cy}{}_2N^{(CH_2)_2OMe}{}_2)]^{2+}$, with a methoxyethyl group on the pendant amine, gives a higher rate of equilibration among the three isomers of the doubly protonated Ni^0 complex (eq 5) compared with the rates of equlibration found in $[Ni(P^{Cy}{}_2N^{t\text{-}Bu}{}_2)_2]^{2+}$ and $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2]^{2+}$; the higher rate is attributed to weakening of the $Ni^0 \cdots H-N$ hydrogen bond by the methoxy group.

In multiproton, multielectron reactions that are pervasive in energy conversion reactions, the question is raised of whether a proton or electron is removed/added first. Deprotonation makes a complex easier to oxidize; similarly, oxidation increases the acidity and lowers the barrier for deprotonation. The removal of a proton and an electron may occur as a proton-coupled electron transfer (PCET) reaction.[32,33] Our experimental work has been complemented by theoretical studies by Hammes-Schiffer and co-workers.[32]

Two pathways have been proposed for the oxidation of H_2 by $[Ni(P^{Cy}{}_2N^{R'}{}_2)_2]^{2+}$. The $[Ni(\eta^2\text{-}H_2)]^{2+}$ and NiH/NH "proton−hydride" intermediates (Scheme 3) are not shown in Scheme 4, which depicts the conversion of $[Ni(P^{Cy}{}_2N^{R'}{}_2)_2]^{2+}$ to the doubly protonated *endo*−*endo* complex. In the "strong base" mechanism, deprotonation of NH^+ by an amine base gives the Ni hydride $[HNi(P^{Cy}{}_2N^{R'}{}_2)_2]^+$, which is followed by oxidation of $[HNi(P^{Cy}{}_2N^{R'}{}_2)_2]^+$ and intramolecular proton transfer from the nickel to the pendant amine. Deprotonation of the NH^+ and oxidation of the Ni^I complex, $[Ni(P^{Cy}{}_2N^{R'}{}_2)_2]^+$, completes the catalytic cycle, regenerating $[Ni(P^{Cy}{}_2N^{R'}{}_2)_2]^{2+}$.

When no exogeneous strong amine base is present, water is not a strong enough base to deprotonate the NH^+. In the "weak base" mechanism illustrated in Scheme 4 for $[Ni(P^{Cy}{}_2N^{(CH_2)_2OMe}{}_2H)_2]^{2+}$, isomerization of the *endo*−*endo* isomer to the *endo*−*exo* isomer is followed by oxidation of the Ni^0 complex. Because of the increased acidity following the oxidation, the NH^+ can be deprotonated by water. Thus, under different conditions, deprotonation and oxidation can occur in either order, though with substantially different overpotentials.

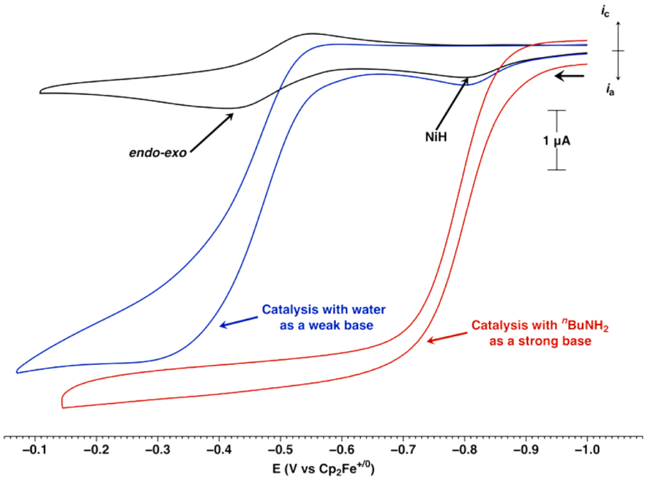


Figure 2. Cyclic voltammograms (MeCN, 25 °C) of 1.0 mM $[Ni(P^{Cy}{}_2N^{(CH_2)_2OMe}{}_2H)_2]^{2+}$ before (black) and after addition of 1 atm H_2 and 5.0 M H_2O (blue) or 1 atm H_2 and 0.2 M *n*-$BuNH_2$ (red). Note the different operating potentials for the strong vs the weak base, indicating different mechanisms.

An ideal catalytic cycle avoids intermediates that are very high or low in energy, so that low kinetic barriers and high rates can be achieved. The doubly protonated Ni^0 *endo*−*endo* complexes lie in a low energy well. Moreover, theoretical studies suggested that only one pendant amine is required for heterolytic cleavage of H_2.[28] Monitoring the reaction of $[Ni(dppp)(P^{Cy}{}_2N^{Bn}{}_2)]^{2+}$ [dppp = 1,2-bis(diphenylphosphino)propane)] with H_2 at −70 °C by NMR spectroscopy gave evidence for a rare Ni^{IV} dihydride in equilibrium with an unusual Ni(0) complex in which both pendant amines are protonated (Scheme 5).[34] At 25 °C, isomerization gives a Ni^{II} hydride with the proton "pinched" in the exo configuration. Oxidation of H_2 catalyzed by $[Ni(dppp)(P^{Cy}{}_2N^{Bn}{}_2)]^{2+}$ is slow (<0.5 s^{-1}) despite a favorable $\Delta G^\circ_{H_2}$ of −4.0 kcal/mol, consistent with the beneficial effect of two positioned pendant amines that assist in the addition of H_2 (Scheme 3) and with the reaction with H_2 being the slow step of the catalytic reaction.

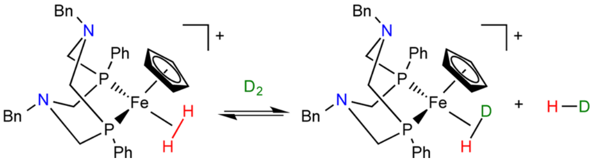
Additionally, we observed that changing from MeCN to a less coordinating solvent increases the rate of H_2 oxidation. In THF, the turnover frequencies for H_2 oxidation by $[Ni(P^{Cy}{}_2N^{Bn}{}_2)_2]^{2+}$ and $[Ni(P^{Cy}{}_2N^{t\text{-}Bu}{}_2)_2]^{2+}$ are approximately 40 s^{-1}. This observation is consistent with MeCN occupying the fifth coordination site, impeding the reaction with H_2.[31]

The catalysts described above are thermodynamically biased to favor H_2 oxidation. One fascinating feature of hydrogenases is that they catalyze the reversible oxidation of H_2.[6,7] We found that $[Ni(P^{Ph}{}_2N^{(CH_2)_2OMe}{}_2)_2]^{2+}$ oxidizes H_2 and also catalyzes the opposite reaction, production of H_2 by reduction of protons.[35] Consistent with the reversibility, the production of H_2 is inhibited in the presence of H_2 (1 atm). The overpotential using this catalyst is low, but the reaction is slow (<0.5 s^{-1}). Subsequent studies by Shaw and co-workers have led to Ni catalysts functionalized with amino acids that exhibit reversible H_2 oxidation in aqueous solution with much higher rates.[36]

■ IRON ELECTROCATALYSTS FOR OXIDATION OF H_2

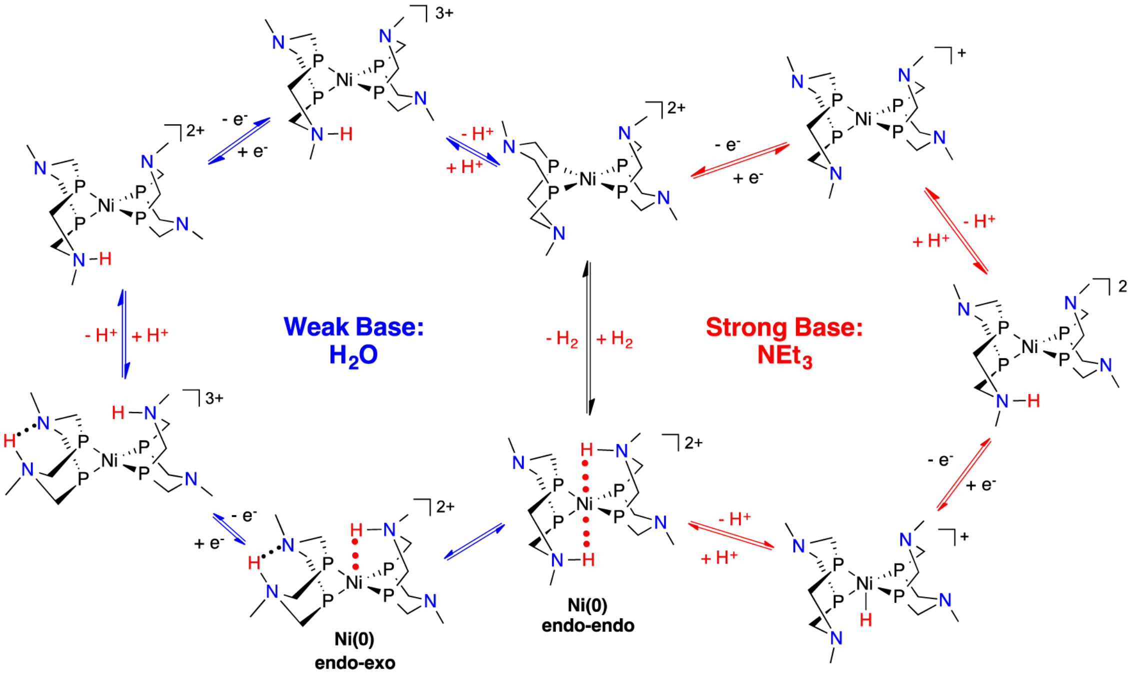
Our studies on Ni complexes illustrate the profound changes in reactivity that can occur when pendant amines are incorporated into a ligand. We sought to apply these principles to the design of molecular electrocatalysts of iron, the most earth-abundant transition metal. Many dihydrogen complexes of iron are stable, suggesting additional divergence from the chemistry of nickel. Iron complexes have been studied in detail as models for the oxidation and production of H_2 by [FeFe]-hydrogenase.[10,37,38]

The dihydrogen complex $[CpFe(P^{Ph}{}_2N^{Bn}{}_2)(H_2)]^+$ was prepared by removal of the chloride from $CpFe(P^{Ph}{}_2N^{Bn}{}_2)Cl$ using $NaBAr^F{}_4$ [Ar^F = 3,5-bis(trifluoromethyl)phenyl] and reaction with H_2 (Scheme 6).[39] Though we originally assigned $[CpFe(P^{Ph}{}_2N^{Bn}{}_2)]^+$ as possessing a vacant coordination site, subsequent studies in our lab have led us to consider the possibility that a pendant amine may be weakly bound. If such

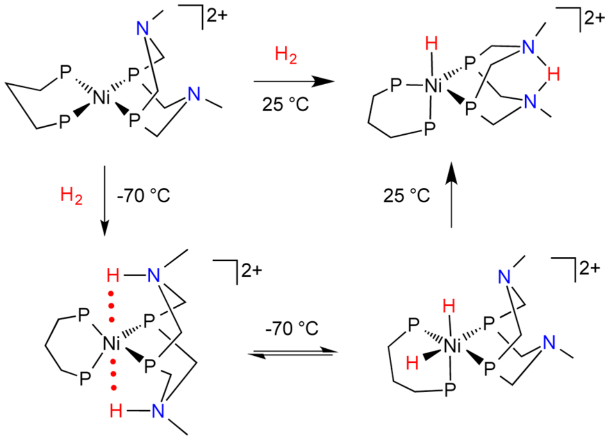


(6)

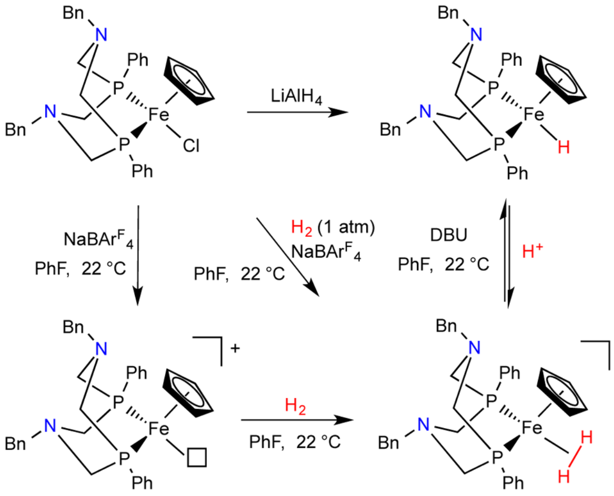
Scheme 4



Scheme 5. Reactions of H_2 with $[Ni(dppp)(P^{Cy}{}_2N^{Bn}{}_2)]^{2+}$ (Organic Groups on P and N Are Not Shown)



Scheme 6



The open square indicates a vacant coordination site

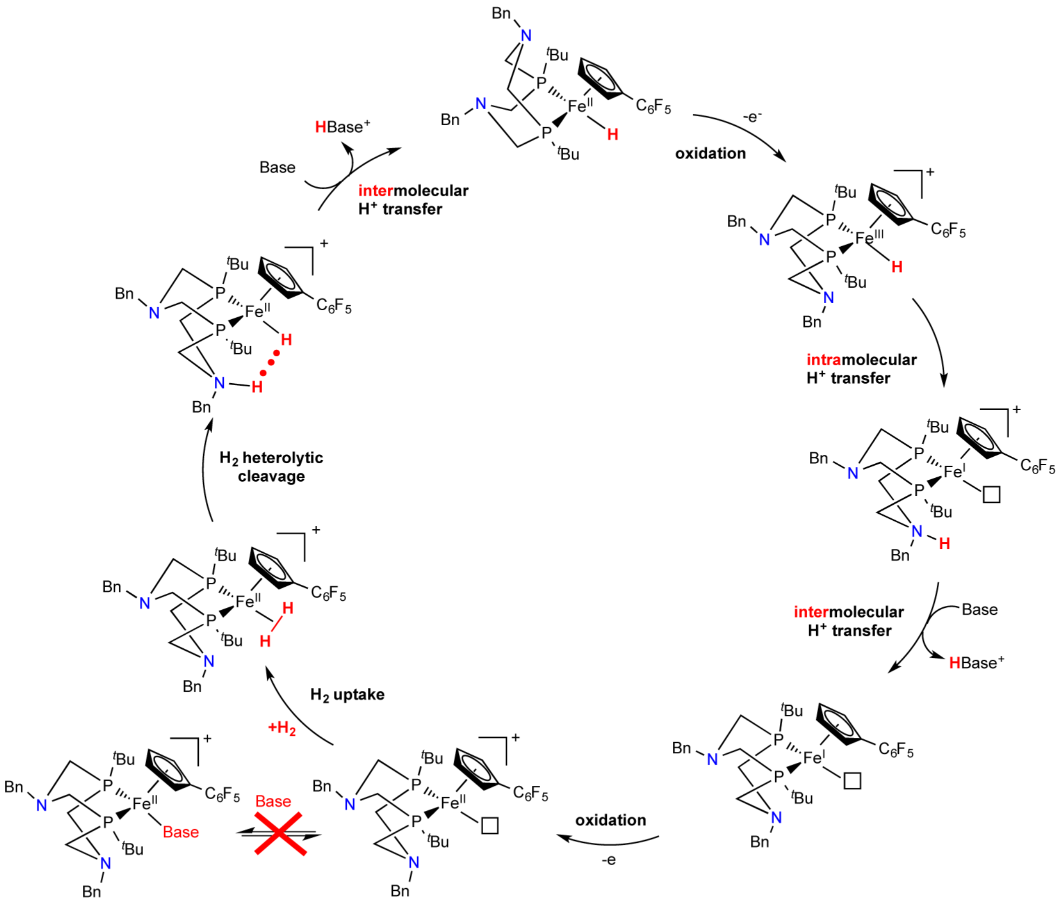
an Fe–N bond does exist, it is weak, as it is readily displaced by H_2 (1 atm).

Addition of D_2 to $[CpFe(P^{Ph}{}_2N^{Bn}{}_2)(H_2)]^+$ gave the H/D scrambled products $[CpFe(P^{Ph}{}_2N^{Bn}{}_2)(HD)]^+$ and HD (eq 6). The HD ligand of $[CpFe(P^{Ph}{}_2N^{Bn}{}_2)(HD)]^+$ was readily recognized in the ^1H NMR spectrum as a 1:1:1 triplet at δ −12.71 (J_{HD} = 30 Hz) due to coupling of H to D, which has spin $I = 1$. Dissolved HD in solution was detected by a triplet (J_{HD} = 45 Hz) at δ 4.22. The key role of the pendant amine was demonstrated by the absence of $Fe(HD)^+$ or free HD in a control experiment with a similar Fe complex lacking any amines. The organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) deprotonates $[CpFe(P^{Ph}{}_2N^{Bn}{}_2)(H_2)]^+$ to give $CpFe(P^{Ph}{}_2N^{Bn}{}_2)H$, a required step in the electrocatalytic oxidation of H_2.

The iron complex $[CpFe(P^{Ph}{}_2N^{Bn}{}_2)(H_2)]^+$ carries out all of the reactions required for catalysis, including binding and cleavage of H_2, electrochemical oxidations, and proton transfers, yet we were disappointed to find no electrocatalysis of H_2 oxidation. The culprit was a competing reaction: DBU binds to $[CpFe(P^{Ph}{}_2N^{Bn}{}_2)]^+$, precluding completion of the catalytic cycle. This attempt to achieve catalysis was, unfortunately, a case of "close but no cigar."

Recognizing the need to design complexes that disfavor binding of the amine base while still promoting facile reaction with H_2 led us to replace the Ph substituents on the phosphorus with sterically demanding *tert*-butyl groups. To increase the acidity of the H_2 ligand, we needed a Cp ligand with an electron-withdrawing C_6F_5 group. Fortunately, Deck developed the synthesis of Cp ligands with C_6F_5 groups,[40] so we prepared $Cp^{C_6F_5}Fe(P^{tBu}{}_2N^{Bn}{}_2)H$. Oxidation of H_2 (1 atm) is catalyzed by $Cp^{C_6F_5}Fe(P^{tBu}{}_2N^{Bn}{}_2)H$ in fluorobenzene at 22 °C using *N*-methylpyrrolidine as the base.[41] The increased current indicating catalytic activity occurs at −0.80 V vs $Cp_2Fe^{+/0}$, which is close to the irreversible peak potential at −0.77 V for

Scheme 7



oxidation of $Cp^{C_6F_5}Fe(P^{tBu}{}_2N^{Bn}{}_2)H$. A turnover frequency of 2.0 s^{-1} was determined, with an overpotential at $E_{cat/2}$ of 160 mV.

The tetrafluoropyridine group (C_5F_4N) is more electron-withdrawing than C_6F_5.[40] For example, the $Fe^{III/II}$ couple for $Cp^{C_6F_5}Fe(P^{tBu}{}_2N^{Bn}{}_2)H$ in fluorobenzene occurs at −0.77 V, while the analogous couple for $Cp^{C_5F_4N}Fe(P^{tBu}{}_2N^{Bn}{}_2)H$ is 70 mV less negative, at −0.70 V.[42] Electrocatalytic oxidation of H_2 (1 atm) in PhF using $Cp^{C_5F_4N}Fe(P^{tBu}{}_2N^{Bn}{}_2)H$ has a turnover frequency of 2.5 s^{-1} (235 mV overpotential) using *N*-methylpyrrolidine as the base. Changing the substituent on the pendant amine from benzyl to *tert*-butyl gives $Cp^{C_5F_4N}Fe(P^{tBu}{}_2N^{tBu}{}_2)H$, which gives a lower TOF (0.5 s^{-1}) using *N*-methylpyrrolidine and a lower overpotential (95 mV). The *tert*-butyl group on the pendant amine makes it a stronger base compared with the benzyl analogue, and even with that change three bonds from the metal, the $Fe^{III/II}$ couples also change. The $E_{1/2}$ of $Cp^{C_5F_4N}Fe(P^{tBu}{}_2N^{Bn}{}_2)Cl$ is found at −0.47 V, while the $E_{1/2}$ of $Cp^{C_5F_4N}Fe(P^{tBu}{}_2N^{tBu}{}_2)Cl$ is 70 mV more negative, at −0.54 V.

In the proposed mechanism (Scheme 7), oxidation of the neutral Fe^{II}−H complex gives a cationic Fe^{III}−H complex with greatly enhanced acidity, facilitating intramolecular proton transfer to the pendant amine. Deprotonation by the exogeneous amine base gives an Fe^{I} complex that is electrochemically oxidized. Binding of the exogenous base is deleterious, clogging up the catalytic cycle, but when the base binding is disfavored, H_2 binding leads to an $[Fe(H_2)]^+$ complex. Heterolytic cleavage of the H_2 ligand, followed by the second intermolecular deprotonation, regenerates the Fe^{II}−H complex, completing the catalytic cycle.

Addition of H_2 to $[Cp^{C_5F_4N}Fe(P^{tBu}{}_2N^{tBu}{}_2)]^+$ gave an orange solution, in contrast to the yellow solutions found for closely related $[Fe(H_2)]^+$ complexes. A single-crystal neutron diffraction study was conducted at the Spallation Neutron Source at Oak Ridge National Laboratory.[43] The short H···H separation of 1.489(10) Å between the hydridic $FeH^{\delta-}$ and the protic $NH^{\delta+}$ (Figure 3) suggests strong "dihydrogen bonding".[44] The structure of this Fe complex provides an idea of how the H−H bond is heterolytically cleaved in the oxidation of H_2 by [FeFe]-hydrogenase. Obtaining this level of precision in an enzyme is difficult because of the challenges in obtaining suitable crystals of natural enzymes, though recent results using ultrahigh-resolution crystallography are quite promising.[45]

Molecular complexes offer the possibility of fine-tuning the thermodynamics by changing the ligands. The complex with a

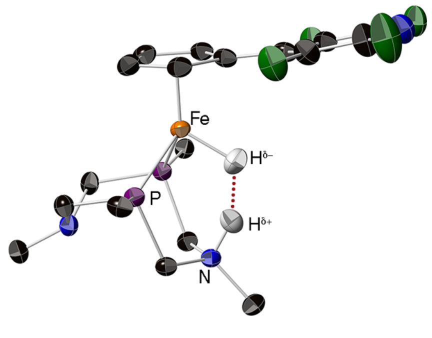
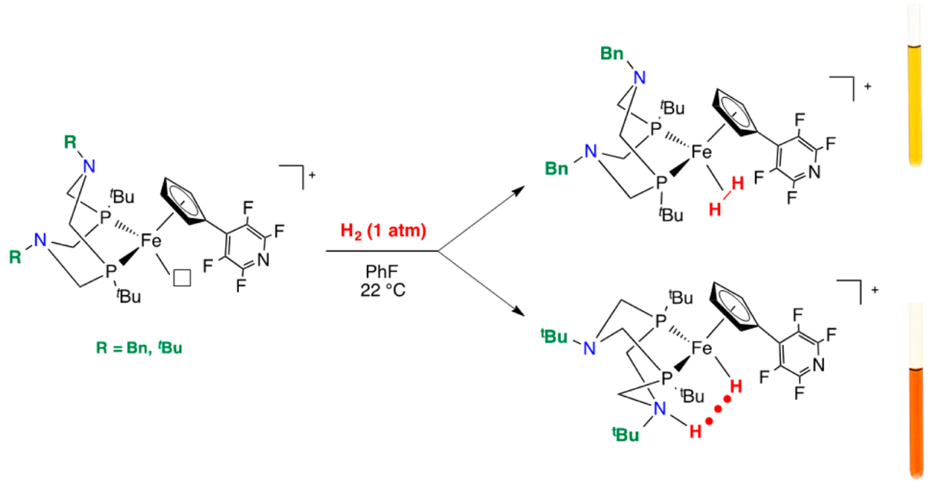


Figure 3. Molecular structure of $[Cp^{C_5F_4N}FeH(P^{tBu}{}_2N^{tBu}{}_2H)]^+$ determined by neutron diffraction.

Scheme 8. Dihydrogen Complex versus Heterolytic Cleavage Caused by a Change in the Organic Group on the Pendant Amine; NMR Tubes of the Two Solutions Are Shown at the Right

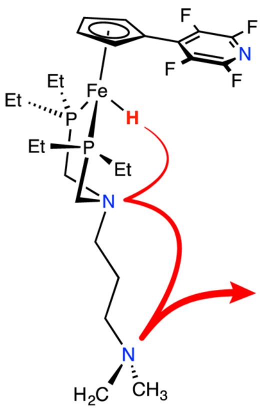


benzyl group on nitrogen is an $[Fe(H_2)]^+$ complex, while the complex with a *tert*-butyl group on nitrogen heterolytically cleaves H_2, forming an Fe−H···N−H complex (Scheme 8).

Related Fe complexes with a flexible PNP ligand exhibit several differences compared with those with the positioned P_2N_2 ligand.[46] Catalytic oxidation of H_2 using $Cp^{C_5F_4N}Fe(P^{Et}N^{Me}P^{Et})(H)$ in PhF using *N*-methylpyrrolidine as the base has a TOF of 8.6 s^{-1} at 22 °C. The higher rate compared with the $Cp^{C_5F_4N}Fe(P^{R}_2N^{R'}_2)H$ complexes is accompanied by a higher overpotential of 410 mV. The cyclic voltammogram of $Cp^{C_5F_4N}Fe(P^{Et}N^{Me}P^{Et})H$ revealed a reversible wave at $E_{1/2}$ = −0.58 V, which is significantly positive compared with the potentials of the $Cp^{C_5F_4N}Fe(P^{R}_2N^{R'}_2)H$ complexes. The reversibility of the wave indicates that proton transfer from the oxidized complex $[Cp^{C_5F_4N}Fe^{III}(P^{Et}N^{Me}P^{Et})H]^+$ is not fast. Experimental and computational studies indicated that the slow steps in the catalytic cycle are the intramolecular Fe-to-N proton transfer and subsequent deprotonation of the protonated pendant amine. Computations revealed that the binding of *N*-methylpyrrolidine is disfavored by about 17 kcal/mol. In contrast, a sterically smaller amine binds to iron, as shown in $[(Cp^{C_5F_4N})Fe(P^{Et}N^{Me}P^{Et})(NH_2{}^{n}Bu)]^+$.[46]

Incorporation of a pendant amine in the outer coordination sphere of the iron complex $[Cp^{C_5F_4N}Fe(P^{Et}N^{(CH_2)_3NMe_2}P^{Et})H]$ (Scheme 9) led a turnover frequency of 290 s^{-1} at 22 °C without an increase in the overpotential compared with $[Cp^{C_5F_4N}Fe(P^{Et}N^{Me}P^{Et})H]$.[47] Experimental and computational studies suggested that the proton is shuttled from the metal to the pendant amine in the second coordination sphere and then to the amine in the outer coordination sphere, where the exogeneous base completes the deprotonation (Scheme 9).

Scheme 9

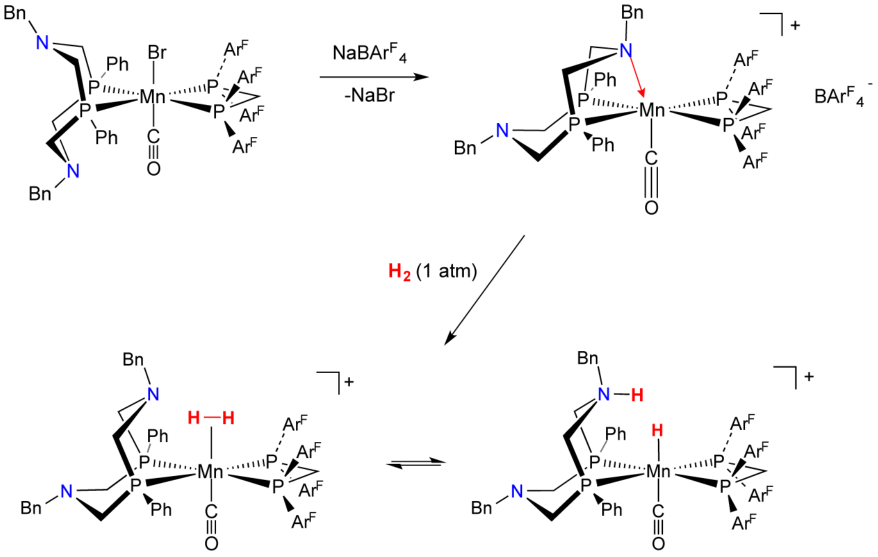


■ MANGANESE COMPLEXES FOR OXIDATION OF H_2

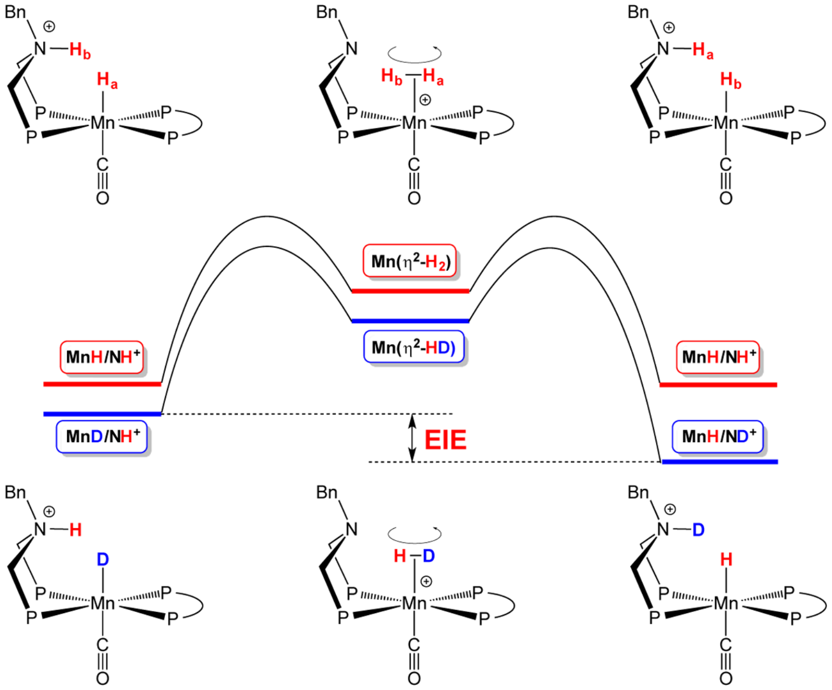
Manganese is earth-abundant but has not been well-studied for oxidation of H_2. Kubas and co-workers reported $[Mn^{I}(diphosphine)_2(CO)]^+$ complexes that bind H_2.[48] We determined K_{eq} = 26 atm^{-1} in PhF solution for reversible binding of H_2 to give $[Mn(P^{Ph}N^{Me}P^{Ph})(dppm)CO(H_2)]^+$ [dppm = bis(diphenylphosphino)methane].[49] The H_2 ligand was not sufficiently acidic to transfer a proton to the pendant amine. A diphosphine with electron-withdrawing aryl groups, $(PAr^{F}_2)_2CH_2$ (bppm), is a weaker donor than dppm, leading to a Mn center that is less electron-rich. Abstraction of bromide from $Mn(Br)(P^{Ph}_2N^{Bn}_2)(bppm)(CO)$ (Scheme 10) gives a cationic Mn^{I} complex that has a κ^3 coordination mode of the $P^{Ph}_2N^{Bn}_2$ ligand, as shown by crystallography.[50,51] The Mn−N bond in this complex is readily (reversibly) displaced by H_2 (1 atm) at 22 °C.

Crystals grown under an atmosphere of H_2 were analyzed by X-ray crystallography, which verified the Mn−H and N−H bonds resulting from heterolytic cleavage. Solution ^{1}H NMR spectra, however, did not reveal resonances diagnostic of Mn−H or N−H groups. Instead, a broad resonance integrating as 2H was observed in the ^{1}H NMR spectrum at δ 2.55, which is approximately the average of the chemical shifts that would be expected for a static structure with Mn−H and N−H bonds. Even at −95 °C the resonance did not "freeze out" into separate Mn−H and N−H peaks. Labeling of the P_2N_2 ligand with ^{15}N gave a triplet of triplets in the ^{15}N NMR spectrum, indicating coupling of the ^{15}N nucleus to two H nuclei as well as $^{31}P-^{15}N$ coupling. These observations, together with additional 2D NMR experiments, provided evidence for reversible heterolytic cleavage of H_2 in this Mn complex. Our estimate of the lower limit for the rate of reversible H_2 cleavage is 1.5×10^4 s^{-1} at −95 °C, and extrapolation to 25 °C leads to an estimated rate of $>10^7$ s^{-1} at 25 °C.

Scheme 10



Scheme 11



Use of HD rather than H_2 provided further evidence for the extremely fast, reversible heterolytic cleavage of H_2. The ^1H NMR spectrum at −20 °C had a resonance at δ −2.78, while the ^2H NMR spectrum exhibited a resonance at δ 7.8. The temperature dependence of the ^1H and ^2H NMR spectra were particularly informative, shifting by >1 ppm in opposite directions (upfield for ^1H and downfield for ^2H) as the temperature was lowered to −70 °C. This temperature dependence reveals a significant equilibrium isotope effect (EIE) that favors the MnH/ND isotopomer over the MnD/NH isotopomer as a result of differences in zero-point energies that dominate the equilibrium (Scheme 11). Preliminary experiments indicated that these Mn complexes catalyze the oxidation of H_2 (1 atm) at 22 °C with an approximate turnover frequency of 3 s^{-1}.

CONCLUSIONS AND OUTLOOK

Incorporating pendant amines into the ligands can produce large increases in rates for oxidation of H_2. In addition to facilitating intramolecular and intermolecular proton transfer reactions, pendant amines provide additional benefits: they promote binding and heterolytic cleavage of H_2, placing the hydride on the metal and parking the proton on the pendant amine. The hydride-acceptor ability of the metal and the basicity of the pendant amine can be altered separately (though not completely independently) by changing the metal and altering the organic substituents on the phosphines and pendant amines. The maximum advantage of using pendant amines is obtained only when the amine is properly positioned to react with the metal hydride or dihydrogen ligand and when the steric and electronic properties of the ligands are optimized

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so that the thermodynamics are tuned to avoid either high-energy or low-energy intermediates.

Our studies of $[Ni(P^{Cy}_2N^{R'}_2)_2]^{2+}$ identified the fundamental principles required for the rational design of molecular electrocatalysts, and these principles were employed for iron and manganese catalysts. A prominent difference in the Ni complexes versus the Fe and Mn complexes is that H_2 complexes are much more stable for Fe and Mn than for Ni. Adjusting both the hydride-acceptor ability of a metal and the basicity of a pendant mine led to remarkably low barriers for reversible heterolytic cleavage of the H−H bond in Mn and Fe complexes. The same principles described here have been used to design molecular electrocatalysts for the opposite reaction, production of hydrogen,[52] and can potentially guide efforts to store and retrieve energy in other chemical bonds, such as C−H or O−H.

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Notes

The authors declare no competing financial interest.

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R. Morris Bullock obtained his B.S. from the University of North Carolina at Chapel Hill, where he worked in Tom Meyer's group. He obtained his Ph.D. at the University of Wisconsin, working for Chuck Casey, and then was a postdoc with Jack Norton at Colorado State University. From 1985 to 2006 he did research at Brookhaven National Laboratory (Long Island, New York). He moved to Pacific Northwest National Laboratory in 2006, where he is a Laboratory Fellow and the Director of the Center for Molecular Electrocatalysis. He is a Fellow of the American Chemical Society and the Royal Society of Chemistry.

Monte L. Helm was born in Fargo, North Dakota. He completed his undergraduate studies in 1995 at Minnesota State University, Moorhead, and his Ph.D. in 2000 at the University of Colorado, Boulder, under the supervision of Arlan Norman. After postdoctoral positions with John Nixon at the University of Sussex (England) and Greg Grant at the University of Tennessee, Chattanooga, he joined the faculty at Fort Lewis College (Durango, Colorado). In 2012 he moved to Pacific Northwest National Laboratory, where he is a research scientist leading the H_2 research in the Center for Molecular Electrocatalysis.

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